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**COMPREHENSIVE ANALYSIS OF MIGRATION  
PATHWAYS (CAMP): CONTAMINANT MIGRATION  
PATHWAYS AT CONFINED DREDGED MATERIAL  
DISPOSAL FACILITIES**

by

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<p>A confined disposal facility (CDF) is a diked enclosure having either permeable or low-permeable walls that are used to retain dredged material solids. There are two types of CDFs, upland and nearshore. An upland CDF is located in an environment that is not inundated by water, while nearshore CDFs are located within the influence of normal tidal or other water fluctuations.</p> <p>A framework for analysis of contaminant migration, cycling, and mobilization pathways is currently being developed to integrate and assess the physical, chemical, and biological processes that occur in CDFs. The framework will use a tiered approach for estimating and predicting mass transport for contaminants in migration, cycling, and mobilization pathways. Contaminant migration pathways are defined as those that allow a</p> <p style="text-align: right;">(Continued)</p>					
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contaminant to leave the confines of the CDF. Contaminant cycling refers to movement of a contaminant in any of its forms between compartments, i.e., sediment to water to organisms, within the confines of a CDF. Contaminant mobilization refers to mechanisms by which contaminants leave a cycle and enter a contaminant migration pathway.

This report identifies and documents key contaminant mobility processes and pathways operative in CDFs under varying operational and environmental conditions. It also summarizes what is known about contaminant migration, cycling, and mobilization pathways, provides information on models and assessment techniques, and identifies areas for which insufficient information is available.

The present information does not permit evaluation of the relative significance of contaminant migration pathways from a CDF. Pathways involving movement of large masses of water, such as CDF effluent, leaching through permeable dikes, or leaching through the dredged material, have the greatest potential for moving significant quantities of contaminants out of the CDF. Pathways such as volatilization may also result in movement of substantial amounts of volatile organic contaminants from CDFs. The relative importance of contaminant cycling and mobilization pathways to net mass balance has not been determined, but available information on each of the contaminant migration, cycling, and mobilization pathways is summarized in the report. Where possible, methods have been provided for making rough estimates of contaminant mass movement via pathways.

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## PREFACE

This report identifies key contaminant mobility processes and pathways for confined dredged material disposal facilities (CDFs) and documents, where possible, methods for estimating the mass movement of contaminants from CDFs. The report was prepared for Headquarters, US Army Corps of Engineers, under the Dredging Operations Technical Support Program (DOTS), managed under the Environmental Effects of Dredging Programs (EEDP) at the US Army Engineer Waterways Experiment Station (WES). Dr. Robert M. Engler is Manager of EEDP and Mr. Thomas R. Patin is DOTS Program Manager. The Technical Monitor for DOTS was Mr. David B. Mathis.

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COMPREHENSIVE ANALYSIS OF MIGRATION PATHWAYS (CAMP):  
CONTAMINANT MIGRATION PATHWAYS AT CONFINED DREDGED  
MATERIAL DISPOSAL FACILITIES

PART I: INTRODUCTION

1. Heavy metals and organic contaminants added to water containing suspended sediments will rapidly become associated with the sediment (Steen, Paris, and Baughman 1978; Suzuki et al. 1979; Voice, Rice, and Weber 1983). This results in contamination of bottom sediments with heavy metals and organic chemical contaminants such as polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs). When dredging and disposal of such sediments occur, the majority of contaminants remain associated with the dredged material. The US Army Corps of Engineers has developed a dredged material management strategy (Francingues et al. 1985), the objective of which is to address testing and disposal of contaminated dredged material. Confined disposal facilities (CDFs) were designed specifically for retention of contaminated material, even though some CDFs, especially those in the Gulf Coast Region, receive uncontaminated material. The possibility that contaminants will disassociate from the solids, leave the CDF, and cause adverse environmental impacts outside the CDF boundaries is a major concern of the Corps when contaminated material is placed in a CDF.

2. A CDF is a diked enclosure having either permeable or low-permeable walls that are used to retain dredged material solids. Two types of CDFs are upland and nearshore, configurations of which are illustrated in Figures 1 and 2, respectively. Figures 1 and 2 also illustrate the major contaminant migration, cycling, and mobilization pathways that will be discussed. The term contaminant migration here refers to pathways that allow a contaminant to leave the confines of the CDF. Contaminant cycling refers to movement of a contaminant in any of its forms between compartments, i.e., sediment to water to organisms, within the confines of a CDF. Contaminant mobilization refers to mechanisms by which contaminants leave a cycle and enter a contaminant migration pathway.

3. Two engineering objectives are of primary importance in the design and operation of either type of CDF; (a) adequate solids storage capacity to

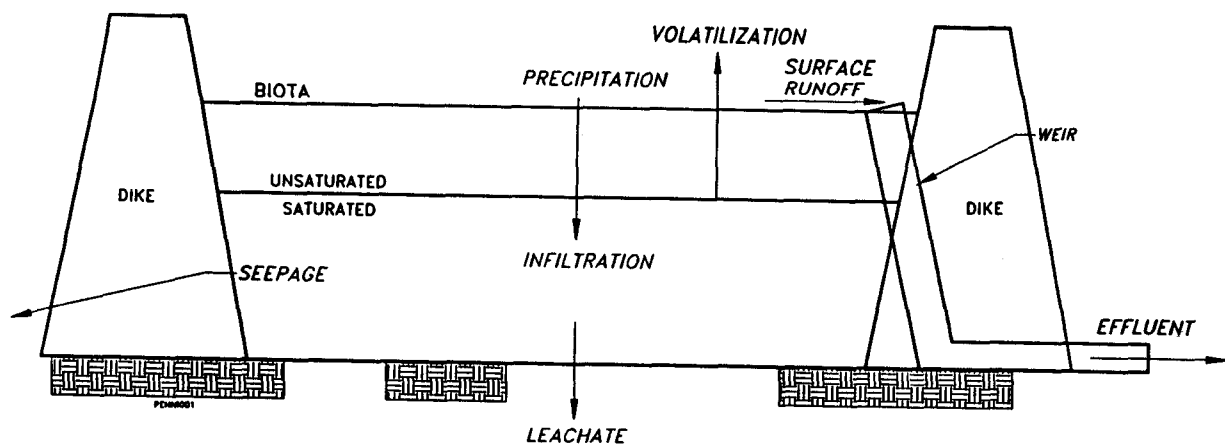


Figure 1. Contaminant migration pathways for upland confined disposal facilities (CDFs)

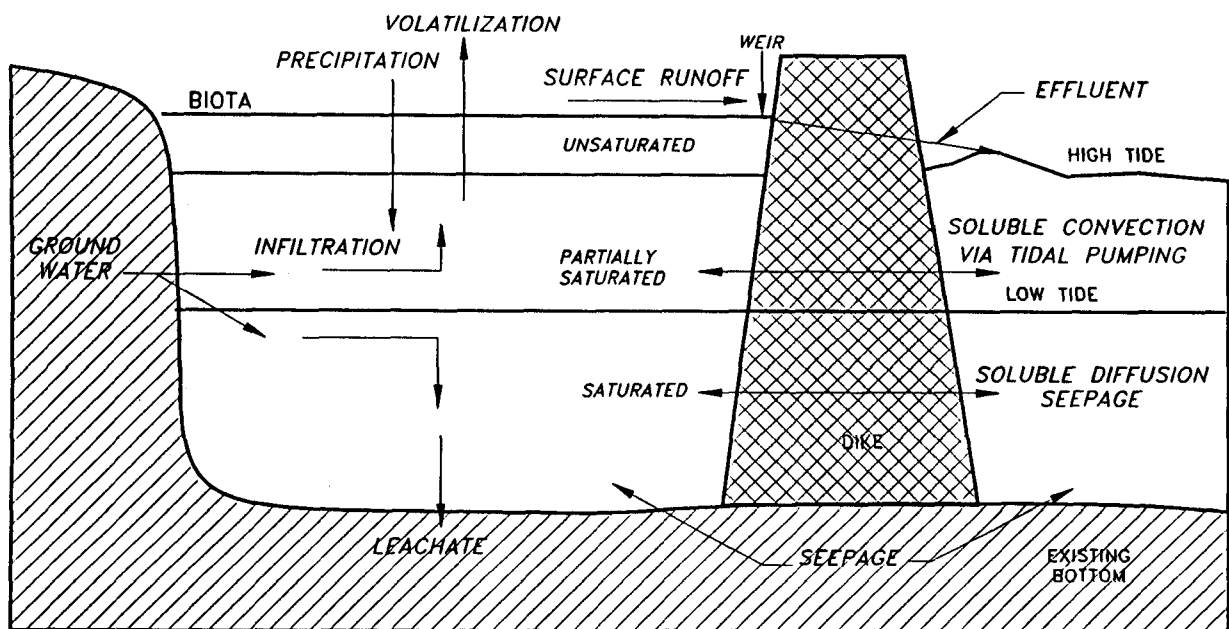


Figure 2. Contaminant migration pathways for nearshore confined disposal facilities (CDFs)

meet long-term dredging requirements, and (b) attainment of the highest possible efficiency in retaining solids during the dredging operation to meet effluent suspended solids requirements (Palermo 1986). Another key element in the design and operation of a CDF is the retention of contaminants, particularly those associated with suspended sediments. Because of the preferential partitioning of contaminants with sediment, significant amounts of contaminants remain associated with sediment during mixing with water (US Army Engineer Waterways Experiment Station (USAE WES) 1987; Myers and Brannon 1988a; Palermo et al. 1989). Guidance for design and management of CDFs to improve hydraulic performance is presented by Shields et al. (1987).

4. A framework for analysis of contaminant migration, cycling, and mobilization pathways is currently being developed to integrate and assess the physical, chemical, and biological processes that occur in CDFs. The framework will use a tiered approach for estimating and predicting mass transport for contaminants in migration, cycling, and mobilization pathways. This report identifies and documents key contaminant mobility processes and pathways operative in CDFs under varying operational and environmental conditions. This report also summarizes what is known about contaminant migration, cycling, and mobility pathways, provides information on models and assessment techniques, and identifies areas for which insufficient information is available.



## PART II: CDF OPERATING CONDITIONS

5. This part of the report presents general descriptions of upland and nearshore CDFs and identifies the contaminant migration, cycling, and mobilization pathways that are present during the various stages of CDF filling and operation. Details of contaminant pathways and operating conditions for each type of CDF are discussed in a later section of the report.

### Upland CDFs

6. Upland disposal in a CDF involves placement of dredged material in environments not inundated by water. Upland sites (Figure 1) are normally dike-confined areas that are hydraulically filled and retain the dredged solids while allowing the carrier water to be released. The clarified carrier water is normally discharged from the upland CDF over a weir.

7. Analysis of contaminant migration, cycling, and mobilization pathways in an upland CDF environment is different because physical and chemical changes begin as soon as the dredged material is placed in the CDF and exposed to air (Peddicord et al. 1986). Once disposal operations have been halted, even if only for a few weeks or months, dredged material consolidation will continue to force pore water out of the dredged material where it can contact the atmosphere and oxidize. After pore water has been removed from the surface of the CDF, the exposed dredged material will oxidize and crack as drying proceeds (Averett et al. 1989). Salt accumulates on the surface of the dredged material where rainfall can dissolve and mobilize the salts in surface runoff. If the dredged material is high in sulfide and low in carbonate, oxidation may result in formation of highly acidic conditions in surficial sediments (Myers and Brannon 1988; Palermo et al. 1989). Volatilization of organic contaminants from exposed sediment is expedited by cracking as the surface dries (Thibodeaux, in preparation).

8. Because of the complexity of the chemical and physical factors affecting the various pathways during the life of an upland CDF, analysis of mass movement of contaminants through a pathway depends to a great extent on prevailing conditions. For this reason, the operating conditions at a CDF and the stage of filling are extremely important variables affecting contaminant migration, cycling, and mobilization pathways. Therefore, three arbitrarily distinguished phases in the life of a CDF are made to facilitate

conceptualization of the many variables involved. The stages are: (a) newly constructed, (b) previously used, and (c) completed.

#### Newly constructed upland CDFs

9. A previously unused upland CDF demonstrates a limited number of contaminant migration, cycling, and mobilization pathways. Migration pathways that exist for this condition include discharges to surface water during filling operations, releases from the settling and dewatering of the dredged material to surface water, leachate or seepage into ground or surface waters, and volatilization to the atmosphere. Contaminant cycling and mobilization pathways are limited to interactions between sediment and water.

#### Previously used upland CDFs

10. Active. In a previously used upland CDF, during active disposal all the migration pathways described for newly constructed CDFs (as well as additional pathways) operate. Additional pathways include surface runoff if exposed dredged material is present, plant uptake, and animal uptake. The incoming dredged material slurry may bury or destroy plants or animals that have become established upon the site, but the pathway will still exist.

11. Inactive. A CDF may be inactive for hours, days, or years. If the time between disposal operations is only a few hours or days, contaminant migration, cycling, and mobilization pathways may not differ substantially from those operative in the previously used CDF during active filling. If the time between disposal operations is months to years, then the environmental conditions at the site will change dramatically and have a pronounced effect on the various pathways. Vegetation and animal communities can become established and plant and animal uptake become cycles that must be quantified. Microbial degradation of organic contaminants may also come into play, especially if an unsaturated zone forms on surficial dredged materials. Surface runoff can also be a pathway for contaminant migration out of the site. The only pathway occurring during active disposal that will not be in effect during this condition is discharges to surface water during filling operations. This occurs because active filling, which is a large source of water to the CDF, has ceased.

#### Completed upland CDF

12. Contaminant migration pathways operating when a CDF is completely filled with dredged material closely parallel those identified in Figure 1. In addition to the contaminant migration pathways, cycling pathways such as plant and animal uptake and microbial degradation will become increasingly

important as means of redistributing contaminants within the site or removing the contaminants of concern.

#### Nearshore CDFs

13. Nearshore CDFs are located within the influence of normal tidal or other water fluctuations. The principal difference between construction of upland and nearshore CDFs is that one or more sides of nearshore CDFs are constructed in the waterway (Figure 2), and the remaining sides are constructed on the shore, use the shoreline, or connect to the shore. The filling process and design for sediment storage and effluent solids control are basically the same as for upland disposal. Nearshore CDFs, like upland CDFs, undergo pronounced physical and chemical changes. The greatest difference between nearshore and upland CDFs is that material in a nearshore site (Figure 2) is completely saturated, or flooded, throughout much of the vertical profile. The saturated dredged material remains anaerobic, which will greatly affect the potential mobility of metals. After the site is either completely or partially filled, the dredged material above high tide or ambient water level begins to dewater and consolidate through movement of water downward as leachate, upward and out of the site as surface runoff, and laterally as seepage through the dike (Averett et al. 1989). The exposed sediment will eventually develop an aerobic surface layer as described for upland CDFs.

14. The bottom of a nearshore CDF below the low-tide or ground-water elevation remains saturated and anaerobic. A transition zone between the aerobic surface layer and the anaerobic bottom layer develops. The transition zone may be alternately saturated and unsaturated as the tide ebbs and floods (Averett et al. 1989). The vertical height of this zone and the volume of dredged material affected depend on the difference in tide or other water elevations and on the permeability of the dike and of the dredged material.

#### Newly constructed nearshore CDFs

15. Contaminant migration pathways that exist for this condition include all of those identified for newly constructed upland CDFs. In addition, transport of contaminants through dike walls is important.

#### Previously used nearshore CDFs

16. Active. Migration pathways operating in nearshore CDFs include all of the pathways discussed for newly constructed nearshore CDFs. In addition, animal uptake, a contaminant cycling and mobilization pathway, may exist if aquatic communities have become established. If the amount of dredged material has reached an elevation above that of the ponded water, contaminant cycling and mobilization by plants may occur.

17. Inactive. Contaminant migration pathways for nearshore CDFs between active periods are the same as those identified for previously used upland CDFs during inactive conditions. In addition, contaminant migration will occur by soluble convection through the dike and by tidal pumping in the ponded water, in the partially saturated zone (if it exists), and by soluble diffusion from the saturated zone through the dike. Ground-water seepage into or through the site can also be a factor affecting contaminant migration.

#### Completed nearshore CDFs

18. When a CDF is completely filled with dredged material, contaminant migration pathways closely parallel those identified in Figure 2. The aerobic, transition, and anaerobic zones in the deposited dredged material become well developed. The site also may become host to a wide variety of plants and animals that may differ from the species present when the CDF was partially filled.

### PART III: CDF INPUTS

#### Dredged Material Inflow

19. The mass of each contaminant added to a CDF can be approximated from dredged material volume and concentration data. However, sediment heterogeneity and widely fluctuating flow rates make such approximations relatively inexact. Accuracy of mass loading estimates can be improved by increasing the number of samples that are analyzed at discharge, but the degree of accuracy needed is unknown at this time.

#### Atmospheric Deposition

20. Atmospheric deposition is a potential source of PCBs and PAHs in CDFs (Callahan et al. 1979; Eadie 1984; and Hallett and Brecher 1984). Most of the existing information on atmospheric deposition of PCBs and PAHs concerns the Great Lakes region (Eisenreich, Hollod, and Johnson 1979; Eisenreich, Looney, and Thornton 1981; Andren and Strand 1981; Eadie 1984). Examination of the PCB and PAH literature for the Great Lakes indicates that the input of these contaminants to the CDF is insignificant compared to the mass of contaminants already present in the dredged material. Eisenreich, Looney, and Thornton (1981) estimated atmospheric deposition of PCBs to Lakes Michigan and Superior to be approximately 80-160  $\mu\text{g}/\text{m}^2/\text{year}$ . Assuming that the density of surface sediment is 1  $\text{g}/\text{cm}^3$ , then the higher rate of PCB deposition would result in the addition of approximately 0.016  $\mu\text{g}$  of PCB for each gram of surface sediment (1-cm depth) into a CDF per year. This deposition of PCBs is higher than that observed for any of the individual PAH compounds reported by either Eadie (1984) or Eisenreich, Looney, and Thornton (1981). Therefore, PCB and PAH additions of this magnitude would be relatively insignificant in terms of overall mass balance and undiscernible from background levels in a CDF containing contaminated dredged material.

21. Atmospheric deposition of metals to a CDF is dependent upon the proximity of the site to sources of airborne metal contamination such as smelters and highways. Therefore, evaluation of metal levels entering a CDF via atmospheric deposition would be a highly site-specific exercise. Results would probably be similar to those found for organic contaminants, i.e., indistinguishable from background in contaminated CDF sediments and soils.

### Contaminated Ground Water

22. In areas where ground water is contaminated, the ground water itself can serve as a source of contaminants for CDFs if the ground water enters the CDF. This occurs if the CDF is situated where the bottom is in the water table or the water table rises due to elevated gradients. Site hydrology will therefore determine if contaminants can be transported into a CDF. Only intensive pre-disposal monitoring of specific sites for hydrology and water quality conditions can provide quantitative estimates of contamination from ground water to the CDF.

#### PART IV: DIRECT CONTAMINANT LOSS PATHWAYS FROM CDFs

23. Direct contaminant loss pathways here refers to those pathways by which contaminants can leave the confines of a CDF. These pathways include effluent, transport of ponded water through permeable dikes, leaching, volatilization of organic contaminants, and surface runoff. Qualitative and quantitative descriptions of these pathways are given, when available, and information needed to complete such descriptions is identified.

##### Effluent

24. Effluent, for either an upland or nearshore CDF, is defined as the product of dredging input and ponded water that leaves the facility by discharge over a weir or through an outlet structure. Effluent consists of both a dissolved component and a suspended sediment solids component. Effluents that are returned to waters of the United States as discharge from a CDF are considered dredged material discharges under Section 404 of the Clean Water Act. Therefore, quality of CDF effluent waters is regulated under State water quality standards (Section 401 State water quality certification) and must be closely controlled.

##### Hydraulic dredging

25. Methods of assessing and predicting the quality of CDF effluent following hydraulic dredging in a previously unused upland CDF have been extensively investigated (Palermo 1986; Palermo and Thackston 1988) and field verified (Palermo 1988). Effluent quality following discharge from hydraulic dredging can be predicted using the modified elutriate test (Palermo 1986). Guidance for use and interpretation of the modified elutriate test is provided in Environmental Effects of Dredging Technical Notes EEDP-04-1 through EEDP-04-4 (Palermo 1985a,b,c,d). A module for CDF effluent following hydraulic dredging is presently being incorporated into the computer model Automated Dredging and Disposal System Management (ADDAMS) (Engler, Patin, and Theriot 1988; Patin and Baylot 1989).

26. Effluent flow from an upland CDF is highest when large quantities of water are being introduced into the CDF during hydraulic dredged material placement. The key to control of suspended solids and associated contaminants and, therefore, water quality of CDF effluent is to design and manage the CDF for solids retention. Design guidance for CDFs is given in EM 1110-2-5027

(US Army Corps of Engineers 1987). Guidance for design and management of CDFs to improve hydraulic performance, thereby increasing water residence time and decreasing suspended solids concentrations in the effluent, is given in Shields et al. (1987).

27. The modified elutriate test mixes dredging site water and sediment. The test is, therefore, not designed to simulate the sediment-water interactions that occur when hydraulically dredged material is introduced into either an upland or nearshore CDF that contains ponded water with contaminant concentrations substantially different from the dredging water being introduced. To accurately predict contaminant water concentrations in such cases, interactions between the hydraulically dredged sediment-water mixture and ponded water must be considered. These interactions are considered in a later part of this report.

#### Mechanical dredging and disposal

28. Although the majority of disposal operations in nearshore CDFs involve hydraulic dredging, mechanical dredging is used at some sites. CDF effluent quality resulting from mechanical dredging and placement of unslurried material differs from that observed from hydraulic dredging because of the limited sediment-water mixing during clamshell dredging. Suspended solids losses from CDF effluent are lower because of reduced mixing and sediment dispersion in conjunction with lower flows during placement of mechanical dredged material. Interactions between sediment and water that occur during placement are related to the surface area of exposed sediment and the velocity at which a discrete cohesive mass of mechanically dredged sediment impacts the ponded water in a CDF. Tests for predicting effluent water quality during disposal of such material have not been developed. Use of interstitial water concentrations to estimate drainage from clamshell disposed material above the water level in the CDF has been suggested, but research in this area is extremely limited. Development of predictive tests for effluent water quality is difficult because of the complexity of simulating mixing between sediment and water when a discrete mass of sediment passes through the water column.

29. The modified elutriate test which was developed for predicting CDF effluent water quality after filling a CDF with material obtained by hydraulic dredging provides unrealistic estimates of contaminant problems for



mechanically dredged material placement.\* Mixing during hydraulic dredging is much greater than in any conceivable mechanical dredging and placement scenario.

30. Thackston recommended breaking the disposal operation for mechanical dredging into component parts, developing laboratory tests for each part, and combining the results mathematically.\* This, or some other approach, must be developed before accurate estimates can be made of the effects of mechanical dredging and placement on effluent water quality in nearshore CDFs. Interim estimates based on modified elutriate results can be used to make worst-case estimates.

#### Transport of Poned Water Through Permeable Dikes

31. Poned water exists in nearshore CDFs until the CDF has been completely filled above the high tide level of the adjacent water body. Upland CDFs are generally built above the ground water table with dikes of low permeability through which minimal seepage is allowed. Therefore, contaminant movement through the dikes in upland sites is usually of minor concern. Transport by ponded water seepage through permeable dikes, however, can be a significant migration pathway for contaminants contained in nearshore CDFs.

32. As was the case with CDF effluent, transport of ponded water through permeable dikes is a direct path for contaminants to leave a CDF. However, unlike the situation for CDF effluent, this pathway exists only as long as the dikes are permeable and ponded water exists on the site. Analysis of saturated sediments adjacent to the dike walls is discussed in the leaching section of this report. Contaminant movement through dikes by seepage is highest during disposal operations when the hydraulic head is highest. At this time, sediment-water interactions also peak and the potential for contaminant mobilization from sediment to water is highest. When a CDF is inactive, sediment resuspension and contaminant diffusion from sediment are the main mechanisms by which contaminants are introduced to ponded water. Therefore, when no disposal is occurring, concentrations of contaminants in the ponded water are expected to be lower than when disposal is active.

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\* Personal communication, 1986, Dr. E. L. Thackston, Professor of Civil Engineering, Vanderbilt University, Nashville, TN.

Contaminant losses  
during active disposal

33. The quality of water exiting a CDF through the dikes depends on the quality of the influent and ponded water, the volume of ponded water, and the sorption properties of the dike material. Much of the information needed to estimate contaminant losses during active disposal does not exist. This is especially true of contaminant interactions with dike materials and of concentration changes in influent and ponded water. Therefore, only simple approaches of limited applicability are presently available to estimate the movement of contaminants through dikes. For contaminants such as ammonium nitrogen or salts contained in saline sediments, the CDF may be modeled as a continuous-flow, complete-mix reactor receiving a nonreactive contaminant.

34. A mass balance using the CDF pond as the control volume yields:

$$\frac{d(C_p V_p)}{dt} = C_d Q_d - Q_o C_p \quad (1)$$

where

$C_p$  = dissolved contaminant concentration in fully mixed pond water, mg/l

$V_p$  = volume of pond, l

$t$  = time

$C_d$  = dissolved contaminant concentration in dredge water, mg/l

$Q_d$  = flow of dredge water into pond, l/t

$Q_o$  = flow of water out of pond, l/t

This equation describes the response of a nonreactive solute in a completely mixed CDF pond to hydraulic disposal of dredged material.

35. To solve Equation 1, data are needed on initial dissolved contaminant concentrations in the pond water and the initial volume of the pond, in addition to the variables identified in Equation 1. Since the pond volume decreases during filling, the rate of change in pond water volume must also be known.

36. For contaminants that undergo significant interactions with suspended solids such as hydrophobic organic compounds and heavy metals, Equation 1 does not apply. For such compounds, the CDF can be treated as a completely mixed reactor in order to develop a simple model for estimating concentrations of dissolved hydrophobic organic contaminants in the pond water. Assuming steady-state, the dissolved concentration in the pond water

for a hydrophobic organic chemical can be estimated using Equation 2 (Thibodeaux, in preparation).

$$C_p = q_o / (K_d + [1/SS]) \quad (2)$$

where

$q_o$  = sorbed concentration in sediment prior to dredging, mg/kg

$K_d$  = equilibrium partitioning coefficient, l/kg

SS = suspended solids concentration in the pond water, kg/l

Note that in Equation 2,  $q_o$  is the sediment contaminant concentration prior to mixing with water. Equation 2 assumes that the suspended solids concentration is constant and the sorbed contaminant concentration of the suspended solids is constant and equal to  $q_o$ . Because such assumptions oversimplify the real system, caution must be exercised when applying Equation 2.

Contaminant losses when  
disposal is not occurring

37. Until a nearshore CDF is filled to where dredged material is above the high tide level in the outside water body, contaminant losses through dikes will continue. Dredged material placed below the pond surface settles to the bottom and consolidates, and dredged material that is placed above the ponded water dries and consolidates. A simple mass balance equation to describe the situation when disposal is not occurring would combine water movement and contaminant concentrations with flow of outside water through the dike into the CDF pond, runoff of precipitation from dredged material above the pond water (mound), seepage from mounded dredged material, and diffusion of contaminants from submerged solids into the ponded water. The situation is more complex, however, than during active disposal because the ponded water mixes with water within the dike before it reaches the water outside the CDF. The dike acts as a physical buffer between the CDF pond and the outside water, dampening the CDF impact on the outside water and vice versa. Several approaches to modeling contaminant losses through the dikes can be applied (Myers, in preparation); however, the data needed to evaluate the various approaches are not available for CDFs.

38. In the operating condition where disposal is not actively occurring, the flow of water into and out of the CDF is controlled by changes in the elevation of the outside water body. Precipitation and evaporation also

influence ponded water flow, but to a much lesser degree. Since the driving force for flow into or out of the CDF is the difference in the water surface elevation between the CDF pond and the outside water body, flow through the dikes can be analyzed using Dupuit's seepage equation. Dupuit's equation gives discharge through a homogenous dike on an impervious base as follows (Harr 1962):

$$q = \frac{k(h_1^2 - h_2^2)}{2L} \quad (3)$$

where

$q$  = discharge per unit length of dike,  $m^3/sec$

$k$  = dike permeability,  $m/sec$

$h_1$  = pond elevation above base of dike,  $m$

$h_2$  = water elevation above base of dike,  $m$

$L$  = horizontal distance separating intersection of dike and pond surface and intersection of dike and water surface,  $m$

39. Runoff and seepage flow from mounded dredged material must be accounted for when determining pond elevation for use in Equation 3. The Hydrologic Evaluation of Landfill Performance (HELP) computer program (Schroeder et al. 1984) can be used to estimate runoff and seepage. The HELP computer model, which has been used successfully for CDFs (USAE WES 1987; Averett et al. 1989), is an advanced, quasi-two-dimensional hydrologic model of water movement across, into, through, and out of landfills. The model accepts climatologic, soil, and design data, and utilizes a solution technique that accounts for the effects of surface storage of water, runoff, winter cover, infiltration, percolation, evapotranspiration, soil moisture storage, and lateral drainage. The program is particularly applicable to CDFs with large areas of dredged material above the ponded water level.

40. Contaminant movement from sediment into ponded water. The dissolved contaminant concentration in seepage from mounded dredged material should be near the pore water concentration of the in-place sediment. Limited data exist on runoff water quality from dredged material, but tests do exist to quantify contaminant concentrations in runoff. This will be covered in more detail in the section on surface runoff.

41. The process(es) that control dissolved contaminant release from sediment in a CDF to the overlying pond water are dependent on sediment

chemistry, overlying water column chemistry and hydrodynamics, and sediment biology. Although significant research has been conducted toward describing the processes affecting exchange rates between sediment-water interfaces, additional information will be needed before predictive methods suitable for routine application are available. The following discussion considers promising conceptual approaches for estimating release of dissolved chemicals from bottom sediments based on chemodynamics. In the first case, control by physical processes associated with water movement (water-side control) is analyzed. In the second case, controls by sediment chemistry are analyzed. In the third case, the impact of activities of sediment biota on mass transfer are discussed, but not analyzed in detail.

- a. Case 1: Water-side control. Movement of chemical A from the sediment to the overlying water column can be modeled as water-side controlled when the resistance to mass transfer is greater in the water column than in the sediment. The physical interpretation of water-side control is that (1) there is little or no resistance to mass transfer in the sediment phase, (2) the sediment is an infinite source of chemical A in which processes operate to continually replenish chemical A at the sediment-water interface, and (3) the movement of chemical A into the water column is limited by mass transfer processes in the water column. This interpretation is approximated when the reactions to produce chemical A in the sediment phase are fast, or chemical A is constantly replenished from below so that there is no gradient in the sediment phase. Ammonia, total phosphate, and orthophosphate releases from sediment during the periods between disposal operations are candidates for this type of analysis.

Assuming that an equilibrium condition has not been reached between the bottom sediment and the overlying water, the concentration of chemical A at some point in the water column far removed from the sediment-water interface will be less than the concentration at the sediment-water interface. Thus, a gradient exists in the water column for mass transfer. This mass transfer process is governed primarily by turbulence associated with water movement.

A simple yet utilitarian equation for water-side control is obtained by defining a water-side mass transfer coefficient as follows (Thibodeaux 1979):

$$F_x = k'_{A2} (C_i - C_w) \quad (4)$$

where

$$F_x = \text{flux, mass/tL}^2$$

$^3k'_{A2}$  = water-side mass transfer coefficient for chemical A across the sediment-water interface, L/t

$C_i$  = chemical A concentration in the interstitial water at the sediment-water interface,  $L^3$

$C_w$  = chemical A concentration in the overlying water at a distance far removed from the sediment-water interface, mass/ $L^3$

The mass-transfer coefficient introduced in Equation 4 is a simplistic way of taking into account the complexities of mass transfer when there is a very thin laminar sublayer at the sediment-water interface and a turbulent zone above the laminar sublayer. The mass transfer coefficient, therefore, depends on the velocity profile that extends from the sediment-water interface into the bulk of the water column. Between disposal operations, surface winds drive water movement in most CDFs. Since these winds vary seasonally in direction and speed, the velocity profile at the bottom and, therefore, the mass transfer coefficient, are constantly changing. It is usually convenient, therefore, to redefine the mass transfer coefficient as an average value applicable over a particular period of time. Thus, the value for the time during ice cover would be different from the value for summer conditions.

Water-side mass transfer coefficients can be obtained experimentally by direct methods or by using one of several correlations based on mass, heat, and momentum analogy theories (Thibodeaux 1979). In the absence of experimental data, estimation of water-side mass transfer coefficients for shallow CDFs carries a high degree of uncertainty because the specific information needed to carry out theoretical calculations is usually not available.

- b. Case II: Sediment-side control, molecular diffusion. For many contaminants of interest, transport processes within the sediment are slow compared to the transport processes above the sediment-water interface. This gives rise to concentration gradients in the pore water with depth in the sediment phase. In the absence of mixing of the upper sediment layer by benthic organisms, bottom currents, and gases evolving from decaying organic matter, the principal mode of contaminant transport in the sediment is molecular diffusion. The flux of chemical A at the sediment-water interface for diffusion-controlled transport is given by Fick's first law as follows:

$$F_x = -D_m \left[ \frac{\partial C}{\partial x} \right]_{x=0} \quad (5)$$

where

$D_m$  = molecular diffusion coefficient for chemical A in water,  $L^2/t$

$\left[ \frac{\partial C}{\partial x} \right]_{x=0}$  = concentration gradient of chemical A in the water at the sediment-water interface, mass/ $L^4$

In order to use Equation 5, the gradient at the sediment-water interface must be determined. One approach widely used in heat and mass transfer studies is to assume that transport in the sediment phase is governed by Fick's second law, the concentration of contaminant at the sediment-water interface is zero, and the initial distribution of contaminant in the sediment is uniform. For these conditions, the semi-infinite diffusion model can be applied to yield the flux to the overlying water through the sediment-water interface as follows (Carslaw and Jaeger 1959):

$$F_x = (D_m C_o) / (D_e \pi t)^{.5} \quad (6)$$

where

$C_o$  = initial concentration of chemical A in the pore water, mass/L<sup>3</sup>

$D_e$  = effective diffusion coefficient of chemical A in the sediment, L<sup>2</sup>/t

$\pi$  = 3.14159.....

The effective diffusion coefficient accounts for tortuosity of the sediment and contaminant sorption by the sediment solids. It can be measured in laboratory studies (DiToro, Jeris, and Ciarcia 1985; Fisher, Petty, and Lick 1983; Formica et al. 1988) or estimated from sediment and chemical properties data alone as follows (Formica et al. 1988):

$$D_e = (D_m t_h) / (1 + K_d \rho_B / n) \quad (7)$$

where

$t_h$  = sediment tortuosity factor, dimensionless

$K_d$  = distribution coefficient for chemical A, L<sup>3</sup>/mass

$\rho_B$  = bulk sediment density, mass/L<sup>3</sup>

$n$  = sediment porosity, dimensionless

The tortuosity factor accounts for the fact that the diffusion path is greater than the distance traveled normal to the sediment-water interface. The correction for tortuosity is usually small and can be approximated by  $t_h = n^{1/3}$  (Formica et al. 1988). The distribution coefficient is usually determined in batch equilibrium tests; for some chemicals, it can be estimated using empirical correlations. For hydrophobic organic chemicals, for example, correlations are available that relate  $K_d$  to the octanol-water partitioning coefficient and sediment organic carbon (Karickhoff, Brown, and Scott 1979; Karickhoff 1981). Given a value for  $K_d$ , the initial pore water contaminant concentration is  $C_s/K_d$ , where  $C_s$  is the initial sorbed concentration. To use Equation 6, an initial time ( $t=0$ ) must be determined at which the concentration of a sorbed chemical is uniform in the sediment.

Calculation of an instantaneous flux has little practical application. A more useful quantity is the average flux over a

given exposure time. Integration of Equation 6 with respect to time yields the following:

$$\hat{F}_x = 2 (D_m C_o) / (D_e \pi t)^{.5} \quad (8)$$

where

$\hat{F}_x$  = gross rate of chemical A entering the water column through the sediment-water interface for the period t

- c. Case III: Impact of biological activities. The previously discussed approaches (Cases I and II) do not take into account bioturbation. Bioturbation is defined for the purposes of discussion in Case III as disturbance of the sediment by benthic organisms that can facilitate transport of contaminants from sediment to water. In harbors and rivers containing polluted bottom sediments the activities of benthic organisms tend to mix the upper sediment layer. In some situations, bioturbation may be more important than diffusion in controlling the flux of contaminants from the sediment to the overlying water. Some simple conceptual models that take into account bioturbation involve treating the affected layer as a completely mixed layer. Other models describe bioturbation with a diffusion coefficient that is corrected for bioturbation for the upper sediment layer. Research in this area is continuing and may eventually provide a mathematical basis for investigating bioturbation in bottom sediments in CDFs. The significance of bioturbation of bottom sediments in CDFs, however, has not been investigated.

42. Information needs. The existing methods for evaluating contaminant transport through dikes yield only crude estimates. Realistic estimates would require much more information because permeable dikes do not act only as hydraulic structures, but undergo chemical and microbial interactions with contaminants. In an unlined CDF, water must move through a tortuous path within the dike. During passage, water and associated contaminants are exposed to significant areas of sorptive surfaces, ranging from crushed limestone and silt-filled voids to microbial slime coatings. This situation is similar to that encountered in a trickling filter. Therefore, dikes potentially adsorb dissolved constituents and may also remove and "treat" dissolved organic constituents in much the same way as attached-growth biological reactors remove and "treat" dissolved organic constituents in wastewater treatment plants. Areas where more information is needed include the following:

- a. A transport model incorporating adsorption/desorption of soluble and partially soluble contaminants.



- b. Exchange of chemicals through the bottom sediment-overlying water interface. Methods for describing the effects of bio-turbation are a particularly pressing need.
- c. Particulate filtering by dikes. Information concerning the factors affecting filtering, especially sealing of the dikes over time by fine-grained material, is needed.
- d. Bioabsorption/biodegradation potential of dike structures.
- e. Mixing zone dynamics in CDFs having permeable dikes. A better description of water flow and mixing within dikes is needed.
- f. Methods for determining the distribution of contaminants between suspended particulates and ponded water.

### Leaching

43. Leaching of contaminants from dredged material in a CDF is a contaminant migration pathway that remains active throughout the life of a CDF. This pathway is only inactive prior to use of the site. The leaching pathway can also be used to estimate seepage from saturated dredged material adjacent to dikes in nearshore CDFs, and may have application for predicting soluble convection from partially saturated dredged material adjacent to dike walls. As the dredged material in a CDF ages, however, the material undergoes physicochemical changes that can affect leachate quality. Dredged material above the water table in a CDF undergoes a transition from anaerobic to aerobic conditions over time. This transition potentially changes both the quantity and quality of leachate. High contaminant concentrations can be generated under oxidized or reduced conditions, or both, depending upon the characteristics of the dredged material and the suite of contaminants contained in the material. For example, if a metal-contaminated dredged material that is low in carbonates becomes acidic via oxidation during aging, metal releases could pose long-term CDF management and treatment problems.

44. Contaminants that move via leachate are transported to the boundaries of the CDF. From there, transport into the environment depends upon contaminant interaction with the soil or lining material that constitutes the CDF boundary. The relationship between leaching and other pathways is presently unknown. Since leaching can move contaminants out of the dredged material, contaminant cycling in pathways such as microbial degradation, plant uptake, and animal uptake could be reduced by lowering the contaminant concentrations resulting from leaching. However, the act of solubilization

into a leachate may actually render a contaminant more susceptible to degradation and uptake.

45. A framework for predicting leachate quality in CDFs has been developed using mass transport theory (Hill, Myers, and Brannon 1988). By applying the principles of mass transport theory, the physical-chemical processes governing leaching have been identified and described mathematically. The mechanisms and factors that can influence and control contaminant transfer from the dredged material solids to the aqueous phase have also been considered in detail. These factors include equilibrium, dissolution kinetics, intraparticle diffusion, and film effects. Hill, Myers, and Brannon (1988) have reviewed state-of-the-art leaching procedures for potential application to dredged material. Various topics related to impacts of sediment chemistry on leaching processes were also reviewed. A sequential batch leaching procedure in conjunction with a column leaching test was recommended for obtaining the coefficients needed in the mass transport equation (Hill, Myers, and Brannon 1988).

46. The recommended experimental procedures for predicting leachate quality have been used to evaluate the potential impacts of confined disposal of dredged material from Indiana Harbor, Indiana; Everett Harbor, Washington; and New Bedford Harbor, Massachusetts (USAE WES 1987; Myers and Brannon 1988a; Palermo et al. 1989). Results are briefly summarized in Technical Note EEDP-02-7 (Myers and Brannon 1988b). Results of test procedures developed by WES were also reviewed at a research needs workshop held at Louisiana State University in 1988 (Louisiana Water Resources Research Institute, in preparation). Workshop panelists were of the opinion that research conducted to date was good and generally validated the basic technical approaches contained in Hill, Myers, and Brannon (1988). However, the consensus was that much research remains to be done before a leach test(s) will be available for routine use.

47. Workshop participants identified the following eight tasks as essential for future research to develop a leach test. These are being actively pursued under the Long-Term Effects of Dredging Operations Program (Engler et al. 1988).

- a. Redesign the column leach test to include thin-layer columns and improved leachate collection systems.
- b. Reevaluate the aerobic column test.

- c. Investigate the impact of colloidal organic matter on interactions between solid and liquid phases.
- d. Determine the role of key parameters such as ionic strength, pH, and contaminant-sediment association on leachate results.
- e. Investigate desorption kinetics.
- f. Investigate techniques for accelerating sediment oxidation.
- g. Develop a more comprehensive mathematical model and verify the model for comparing batch and column test results.
- h. Verify test protocols in a field situation, preferably at a multiagency national research site.

48. As the preceding recommendations for research tasks illustrate, much work remains to be done before routine leachate tests can be recommended for use. However, crude estimates of anaerobic leachate quality and quantity can be obtained now by using contaminant concentrations from either interstitial water or the initial batch leach cycle in conjunction with water balances from the HELP model. The approach has not been used for aerobic dredged material, but could be if the HELP model were used in conjunction with batch test results.

#### Emission of Volatile Contaminants

49. When contaminated dredged material is placed in a CDF, the potential exists for volatile organic chemicals associated with the sediment to be released to the air. The emission process is termed volatilization, and is potentially significant under some environmental conditions. Volatile emissions are a pathway for direct loss of contaminants from a CDF that can impact other contaminant pathways by removing contaminants from the CDF system. For example, volatile loss can affect the amount of contaminant subject to leaching, microbial degradation, plant uptake, and other processes. Brannon and Myers (unpublished data) have shown that up to 27  $\mu\text{g}/\text{m}^2/\text{hr}$  of PCB Aroclor 1242 could be lost to the atmosphere through volatilization from New Bedford Harbor sediments.

50. Theoretical models for evaluation of volatile emissions from CDFs to air during dredged material disposal are currently being published (Thibodeaux, in preparation). Thibodeaux identified four primary vapor phase transport emission locales for various CDF designs and stages of filling. The first volatile emission locale is related to sediment handling, e.g., dredging, transporting, discharging, and related operations. The remaining three

are comprised of (a) exposed and drying sediment beds devoid of vegetation, (b) that portion of the CDF that contains water, and (c) sediment that is covered with vegetation.

51. Thibodeaux (in preparation) presents vignette models that describe theoretical volatile emission losses from the four emission locales. Appendix B in Thibodeaux's report also provides initial PCB vaporization estimates for emissions during sediment handling (CDF filling with a submerged diffuser), emissions from exposed sediment, and emissions from capped contaminated sediment (a variation of the exposed sediment emission locale) for the pilot-scale CDF alternative for New Bedford Harbor. Thibodeaux calculated that the relative ratios of volatile PCB losses from a CDF occur in the order: exposed sediment > ponded sediment > capped sediment. This suggests that volatilization will be most significant during the time when a CDF is actively receiving dredged material and sediment is exposed. Preliminary laboratory results for volatilization from exposed sediment (Brannon and Myers, unpublished data) agree with this theory, but the resultant volatile losses were lower than those based on the theoretical calculations of Thibodeaux. The following equation (Thibodeaux 1989) describes volatilization of organic compounds (VOCs) from exposed sediment:

$$n_A = \frac{\left[ \frac{w_A H_p}{K_d} - \rho_{A1} \right]}{\left[ \frac{\pi t}{D_{A3} \left( \epsilon_1 + \frac{K_d \rho_B}{H_p} \right)} \right]^{1/2} + \frac{1}{3k'_{A1}}} \quad (9)$$

where

- $n_A$  = emission flux of VOC A, g/cm<sup>2</sup>/hr
- $w_A$  = concentration of VOC A on sediment solids, g/g sediment
- $H_p$  = Henry's constant, cm<sup>3</sup> water/cm<sup>3</sup> air
- $K_d$  = distribution coefficient, cm<sup>3</sup> water/g sediment
- $\rho_{A1}$  = concentration of VOC A in background air, g/cm<sup>3</sup>
- $t$  = time sediment has been exposed, hr
- $D_{A3}$  = diffusion coefficient of VOC A in air-filled pores, cm<sup>2</sup>/hr
- $\epsilon_1$  = air-filled porosity, cm<sup>3</sup>/cm<sup>3</sup>
- $\rho_B$  = bulk sediment density, g sediment/cm<sup>3</sup> sediment

<sup>3</sup>k'<sub>A1</sub> = air-side mass transfer coefficient, cm/hr

52. Mechanisms governing volatile emissions from standing water are relatively simple compared with volatile emissions from the other locales. Therefore, the model for exposed sediments can also be used to obtain a crude estimate of volatile emissions from standing water in a CDF (Thibodeaux, in preparation). The equation for making such predictions is as follows:

$$n_A = {}^1K'_{A2} \left[ \left( \frac{w_A}{K_d + 1/P_{32}} \right) + P_{A2}^{**} \right] \quad (10)$$

where

<sup>1</sup>K'<sub>A2</sub> = overall liquid phase mass transfer coefficient, cm/sec

P<sub>32</sub> = concentration of suspended solids, kg/l

P<sub>A2</sub><sup>\*\*</sup> = hypothetical concentration of VOC A in water for a background VOC concentration in air of ρ<sub>A1</sub>, g/cm<sup>3</sup>

Assuming that the background VOC concentration in air is zero, then P<sub>A2</sub> is also zero.

53. Use of models to predict longer term volatile emissions from ponded water and exposed sediment cannot now be justified. None of the volatile emission models have been verified for contaminated sediment in CDFs (Thibodeaux 1989). However, the modeling approach used by Thibodeaux has been verified for volatile organic compounds from "land farming" of sludge (Eklund, Nelson, and Wetherold 1987). The Chicago District has also used the modeling approach of Thibodeaux to examine the relative significance of volatilization for various operational schemes related to dredging and disposal of contaminated dredged material for the Indiana Harbor Draft Environmental Impact Statement. Using this approach, a ranking of potential PCB mass flux for different disposal options was determined and options were evaluated against each other. The modeling approach used by the Chicago District considered only the "exposed sediment void of vegetation," and "ponded zone" locales as emission sources for PCB flux.

54. Additional information is required before contaminant volatilization can be predicted with confidence. Laboratory test procedures must be developed beyond the first generation experimental apparatus that now exists. Refinement in laboratory procedures will allow better integration of

laboratory results and transport mechanism equations permitting field verification of critical transfer coefficients and an ability to confidently predict volatile emissions.

### Surface Runoff

55. Surface runoff can be a direct pathway for contaminant loss from upland and nearshore CDFs. This is especially true when site closure is near or the site has been closed and runoff is discharged directly through the outlet structure. Management practices such as ditching to promote dewatering may increase the severity of surface runoff by increasing the effective surface area and channeling water flow. Surface runoff can also impact ponded water by serving as a source of contaminants when dredged material rises above the water level in a nearshore CDF.

56. Empirical methods presently exist for assessing the quality of surface runoff (Lee and Skogerboe 1984; Skogerboe and Lee 1987). The WES Rainfall Simulator-Lysimeter System has proven to be effective in predicting surface runoff water quality from proposed dredged material disposal sites. Material placed in the system can be evaluated under the predominately anaerobic sediment conditions that prevail when the dredged material first becomes exposed in the CDF. Runoff characteristics of dried and oxidized material that can exist in an older CDF can also be evaluated as can intermediate conditions of sediment oxidation.

57. Initial studies have been conducted for Indiana Harbor sediment (USAE WES 1987) on development of a simplified laboratory test to screen sediments that may cause adverse environmental problems with surface runoff. If the screening tests indicate the potential for adverse environmental impacts, the sediment is brought to WES for evaluation in the Rainfall Simulator-Lysimeter System. However, the screening tests have not been fully developed. Other methods for evaluating runoff and seepage from mounded dredged material in a CDF have been previously discussed in the runoff section for transport through permeable dikes.

58. Information needed in this area includes development of a screening test or a combination of short-term laboratory tests coupled with mathematical models to predict the mass of contaminants mobilized by surface runoff under varying conditions of sediment geochemistry (e.g., stages of drying, oxidation). The factors affecting resuspension of exposed dredged material during

rainfall events must also be investigated. In addition, existing data for transport of soluble and particulate sorbed contaminants from dredged material during rainfall events should be evaluated using the HELP model.

## PART V: INDIRECT CONTAMINANT LOSS PATHWAYS

59. Indirect contaminant loss pathways are those through which contaminants move from one compartment to another, and may if conditions are right, enter a direct contaminant loss pathway. For example, plant uptake of contaminants from deeper CDF sediment may result in translocation of contaminants into plant foliage which eventually returns to the sediment surface as leaves fall. As a part of the surface litter, the contaminants may enter into another cycle such as a food chain. Animals living in and feeding upon the litter can become contaminated and, subsequently, be consumed by a predator capable of leaving the site. The contaminant associated with the plant material may also be washed or leached into ponded water where it may ultimately leave the site through dike seepage. This is a form of surface runoff from the dredged material and illustrates the dual position of surface runoff in a CDF; a contaminant migration pathway and/or a contaminant mobilization pathway. The role of surface runoff as a contaminant migration pathway has been discussed previously. Surface runoff acts as a contaminant mobilization pathway in a nearshore CDF when the CDF is inactive and ponded water is present. Contaminant mobilization occurs as a consequence of surface runoff when sediment is moved into the ponded water where sediment-water interactions can then occur, resulting in a possible increase in dissolved contaminant concentration in the ponded water.

60. Interactions of internal contaminant cycles with direct loss pathways are very complex and, in most cases, not completely understood. The relative importance of indirect contaminant loss pathways is virtually unknown.

### Interaction of Suspended Solids With Ponded Water

61. For contaminants and situations that are not amenable to simplified approaches, more complex methods for predicting and describing the transfer of contaminants from the solid to the liquid phase may be needed. Such approaches may also be needed to provide long-term solutions to the sediment-water interaction problems that affect many different contaminant migration pathways in a CDF.

62. Existing procedures for predicting the interactions between contaminants associated with suspended solids and water are primarily



empirical. Empirical procedures include the previously discussed modified elutriate test that allows predictions of CDF effluent quality to be made for hydraulic dredging. However, as useful as empirical procedures are, inter-phase contaminant transfer between suspended sediment and water must be understood before a comprehensive model of mass loss of contaminants from CDFs can be made.

63. The impact of suspended particulates in ponded water will be most significant during active filling of the CDF when sediment and water mixtures are being disposed. In an inactive CDF containing ponded water, suspended sediments are not being introduced into the water on a massive scale and resuspension of deposited sediment and surface runoff from emergent sediment are the major sources of suspended solids. Resuspension of deposited sediment depends on the height of the ponded water column and the energy regime (Rosa, Nriagu, and Wong 1983) while surface runoff depends on the area of exposed sediment and rainfall. As the CDF is filled, the volume of ponded water decreases and the relative impacts of suspended solids decrease. When a CDF is completely filled, ponded water is no longer a contaminant loss pathway.

64. Suspended sediment/water interactions are difficult to model because of the complex nature of sediment (Brannon et al. 1976) and the sediment-specific interactions that contaminants exhibit (O'Connor and Connolly 1980). The complexity of the sediment matrix makes prediction of the adsorption/desorption behavior of contaminants associated with sediments a difficult task in the absence of empirically derived data, especially for metals. These difficulties are increased when the properties of the water and contaminants to which sediment is exposed are considered.

65. All of the methods used to describe suspended sediment/water interactions to date are variations of either equilibrium or non-equilibrium approaches. Equilibrium processes are controlled by thermodynamics and may involve mass transfer, while non-equilibrium processes involve reaction kinetics as well as mass transfer (Bird, Stewart, and Lightfoot 1960; Thibodeaux 1979; Geankoplis 1983). Results of many studies (Garcia-Miragaya and Page 1976; Loganathan, Burau, and Fuerstenau 1977; Shuman 1977; Adams and Sanders 1984; Trefry and Metz 1984; LaFlamme and Murray 1987; Neal et al. 1987) strongly suggest that either equilibrium distribution coefficients or kinetic rate constants for a specific system be obtained prior to modeling under environmental conditions that mirror those at the site. A detailed discussion and derivation of equilibrium and non-equilibrium distribution

coefficients between sediment and water can be found in Hill, Myers, and Brannon (1988).

66. Recent studies (Jannasch et al. 1988; Nyffeler et al. 1984; Nyffeler, Santschi, and Li 1986; Santschi 1984; Santschi et al. 1986) indicate that an equilibrium approach may not be valid for locations with high particle turnover rates, such as an active CDF. In areas of rapid particle removal, residence times may be insufficient to allow sorption reactions to reach equilibrium (Jannasch et al. 1988). Residence time of particles is therefore a very important variable in contaminant-water interactions, especially in environments where reaction times of contaminants with particles are greater than or equal to particle residence time (Jannasch et al. 1988).

67. Nonequilibrium processes have also been examined in detail by Hill, Myers, and Brannon (1988). Rate processes must be used to describe sediment-water interactions in nonequilibrium situations. However, rate processes are much more complex than equilibrium approaches because they require knowledge of elementary reaction pathways and their rate constants (Nyffeler, Li, and Santschi 1984). Therefore, modeling of the time-dependent distribution of contaminants into water and sediment is generally empirical in nature, because such an approach summarizes the complex interactions of dissolved and particulate forms of the contaminants (Nyffeler, Santschi, and Li 1986). For a more rigorous investigation of trace element cycling, an understanding of trace element speciation as well as all reactions of the dissolved element with the solid phase and its surface would be necessary (Nyffeler, Santschi, and Li 1986). Such an approach is beyond present capabilities.

68. Bird (in preparation) evaluated numerous modeling approaches, including simplified calculation techniques, mixed reactor and simplified riverine models, fugacity models, MINTEQA1, EXAMS/MEXAMS, TOXIC, HSPF, TOXI4, SERATRA, FETRA, and TODAM for applicability to dredged material and dredged material disposal. Bird concluded that tailoring of some of the modeling approaches for direct application to Corps problems could be done with modest resources. For CDFs, Bird concluded that a TOXI4-based CDF model could be expanded into a framework for a more comprehensive analysis of losses from a facility. TOXI4 was modified by Martin, Ambrose, and McCutcheon (1988) to model exposure concentrations and releases from CDFs in the Great Lakes.

69. TOXI4 is a version of the Water Quality Analysis Simulation Program-4 (WASP4) that is designed to simulate organic chemicals and heavy metals (Ambrose et al. 1988). TOXI4 was created by adapting the kinetic

structure of EXAMS-II (Burns, Cline, and Lassiter 1982; Burns and Cline 1985) to the transport framework of WASP4 and adding sediment balance algorithms. Martin and McCutcheon (in preparation) have reviewed the factors influencing exposure concentrations and release of organic contaminants from CDFs as well as modeling approaches such as TOXI4 that may be used to estimate that exposure and release.

70. Refinement of existing models will require that additional information concerning sediment/water interactions be obtained, especially at the relatively low suspended solids concentrations that would be expected in ponded water. Development of site-specific tests may be required in order to predict the effects of resuspension of solids on contaminant mobility. Existing models that address mixing and mass transport in conjunction with contaminant adsorption/desorption will require expansion, validation, and field verification.

#### Degradation of Organic Contaminants

71. Organic contaminants, such as PCBs, PAHs, and pesticides, that are often present in dredged material are a cause of concern for regulatory agencies and the general population. Degradation of organic contaminants, mediated through either microbial activity or hydrolytic and/or photolytic reactions, has the potential to significantly reduce levels of organic chemicals in CDFs. Information exists on microbial degradation of natural and manmade organic substances (see, for example, Crawford (1981); and Chakrabarty (1982)). Among the groups of compounds that have been studied are: PCBs (Hankin and Sawhney 1984; Focht and Brunner 1985; Brown et al. 1987; Fairbanks, O'Connor, and Smith 1987; Roberts 1987), petroleum and PAHs (Cerniglia and Gibson 1978; Herbes and Schwall 1978; Kiyohara and Nagao 1978; Dibble and Bartha 1979; Cerniglia, Gibson, and Van Baalen 1980; Ensley, Gibson, and Laborde 1982; Readman et al. 1982; Schoken and Gibson 1984; Mihelcic and Luthy (1988a,b), phenol (Dobbins et al. 1987), and other substances (Johnson and Heitkamp 1984; McGinnis et al. 1989). Many of these compounds are common contaminants in CDFs.

72. Microbial degradation in CDFs may occur under aerobic, anaerobic, or alternating aerobic/anaerobic conditions. Aerobic pathways are generally the most efficient and rapid means of breakdown, often resulting in complete mineralization of contaminants to their basic inorganic components, i.e., CO<sub>2</sub>,

$\text{NO}_3$ , or  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . However, anaerobic conditions prevail in most contaminated sediments that remain saturated.

73. Under anaerobic conditions, the complete mineralization of organic contaminants often observed under aerobic conditions may occur partially or not at all. A myriad of intermediate products such as volatile and non-volatile fatty acids and alcohols, saturated hydrocarbons, other reduced organic compounds, methylated metals, and ammonium may be formed. In general, most anaerobic pathways are not efficient mechanisms for degrading organic contaminants. Recent studies indicate that methanogenic fermentation, an anaerobic pathway, may be responsible for the degradation of several oxygen-substituted aromatic compounds, including: aromatic acids, aldehydes, alcohols, phenols, catechol, trihydroxylated benzenoids, plus halogenated aromatic acids and phenols (Gribic-Galic and Vogel 1987). Aromatic hydrocarbons such as toluene and benzene may also be anaerobically transformed by mixed methanogenic cultures derived from sewage sludge enrichments. However, the utility of this pathway is limited in cold regions because methanogenesis occurs slowly or not at all at temperatures below  $10^\circ\text{C}$  (Mallard and Frea 1972). Anaerobic conditions also appear to be necessary for portions of other degradation pathways to function. Degradation of PCBs, for example, appears to be a two-step process wherein dechlorination occurs under anaerobic conditions and is followed by oxidative biodegradation in aerobic environments (Brown et al. 1987).

74. One microbial degradation process that may occur under either aerobic or anaerobic conditions is cometabolism (Horvath and Alexander 1970). In cometabolism, a compound is partially broken down because of similarity to a natural substrate normally used by the organism. However, the organism initiating decomposition is unable to completely degrade the compound and thereby gains little or no energy from the process. Any additional degradation of the partially degraded contaminant must then be carried out by other microorganisms. The relative importance of cometabolism to contaminant cycling is not known.

75. Chemical and physical processes also affect the level of organic contaminants present in the environment. Organic matter present in aquatic ecosystems, for example, can affect the physical state and environmental fate of organic contaminants. Humic substances exert influences through:

(a) increasing the apparent water solubility of nonpolar compounds (Wershaw, Burcar, and Goldberg 1969; Ogner and Schnitzer 1970a,b; Ballard 1971; Matsuda

and Schnitzer 1973; Hassett and Anderson 1979, 1982; Boehm and Quinn 1973; Mathur and Morely 1978; Landrum et al. 1984); (b) binding of organic compounds through covalent bonds, charge-transfer complexes, hydrogen bonding, or Vander Waals interactions (Paris, Wolfe, and Steen 1982; Perdue 1985); (c) hydrolyzing pesticides (Perdue 1983); (d) photosensitizing contaminants (Zepp, Baughman, and Schlotzhauer 1981 a,b); (e) altering bioavailability of contaminants to aquatic organisms (Leversee et al. 1983); and (f) controlling the rate and extent of biodegradation of organic contaminants at low levels (Holm et al. 1980; Novick and Alexander 1985; Schmidt and Alexander 1985). Several studies have examined the effects of dissolved humics on the hydrolysis of organic contaminants. Humic and other organic acids have been observed to cause hydrolysis of atrazine (Li and Felbeck 1972a,b; Khan 1978a,b), alkyl esters of 2,4-Dichlorophenoxyacetic acid, and other hydrophobic organic compounds (Perdue and Wolfe 1984). Other studies have examined the influence of natural organic materials on the photolysis of certain chemicals (Ross and Crosby 1975; Zepp et al. 1975, 1977; Zepp, Baughman, and Schlotzhauer 1981a,b; Mills et al. 1982). Examples of chemicals so affected include disulfoton, 2,5-dimethylfuran, aniline, and cis-1,3-pentadiene, all of which are photosensitized in the presence of humic and fulvic acids (Zepp, Baughman, and Schlotzhauer 1981a,b). Photolysis rates are variable, however. For example, at low dimethylfuran levels, first-order reactions occur and the reaction rate constants are directly proportional to both average light intensity and the concentration of humic substances.

76. Most dredged material placed into a CDF originates from reducing environments. Dredging and disposal operations would not be expected to substantially alter anaerobic pathways because the dredging and filling process does little to change the reducing nature of the sediment. Placement of the material into a warmer CDF environment may accelerate some anaerobic degradation processes, particularly methane fermentation. Acceleration of biodegradation in anaerobic sediment may also possibly be attained by addition of alternate electron acceptors, such as nitrate.

77. Many interactions may occur between degradation pathways resulting from microbial, hydrolytic, and photolytic activities, and indeed, between aerobic and anaerobic microbial pathways. Furukawa (1982) has reviewed degradation pathway interactions for PCBs. The review showed that PCBs are decomposed when exposed to ultraviolet light. In addition, PCBs react to light mainly by stepwise dechlorination (replacement of chloride by hydrogen

in aqueous and organic media. Photolytic dechlorination may remove small, but significant, amounts of chlorine annually from PCBs in shallow waters. Photolysis in conjunction with microbial degradation in the same environment may produce rapid, efficient decomposition of PCBs with both high and low chlorination in surface sediments exposed to sunlight. Whether or not these same processes work synergistically to degrade other organic contaminants is not known at present.

78. Formation of many intermediates in anaerobic degradation pathways can be anticipated based on what is presently known about existing pathways. However, the concentration and exact complement of intermediates present at any one moment vary and are difficult to predict, especially if more than one contaminant is present and multiple pathways occur simultaneously. When aerobic conditions become established in sediment surface layers, aerobic degradation products ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and nitrate) form. Some of these products may leave the site, while those remaining are recycled to primarily simple inorganic forms that have few, if any, toxic impacts.

79. Predicting degradation products and rates is difficult, although some means of estimating products and rates of individual compounds are available. Suitable predictive methods that may be applicable to CDFs exist in the literature. For example, prediction of biodegradation potentials for organic compounds in soil uses the rate of uptake and/or mineralization of radiolabelled substrates by natural microbial communities. Various modifications of this procedure have been used in water, soils, and sediments to determine heterotrophic potential (Wagner 1975; Pfaender and Bartholomew 1982; Ferroni, Leduc, and Winterhalder 1985; Dobbins et al. 1987). Dobbins et al. (1987) used the procedure to study phenol degradation in soil. Pfaender and Bartholomew (1982) applied the method to measurement of aquatic biodegradation rates for m-cresol, chlorobenzene, nitrilotriacetic acid, and 1,2,4-trichlorobenzene. Fairbanks, O'Connor, and Smith (1987) examined mineralization and volatilization of PCBs in sludge-amended soils and used radiolabelled compounds to compute first-order volatilization and  $\text{CO}_2$  evolution rate constants.

80. Existing mathematical models may also contain microbial degradation subroutines. The WASP4 system (Ambrose et al. 1988) contains a toxic chemical model, TOXI4, that has provision for hydrolysis, photolysis, and bacterial degradation. TOXI4 uses first-order biodegradation rate constants or half-lives for the water column and benthos. If first-order rates are unavailable,

or if they must be extrapolated to different bacterial conditions, then a second-order approach is used. In TOXI4, hydrolysis by specific-acid-catalyzed, neutral, or basic pathways is considered for the various species and phases of each chemical. Reaction coefficients are specified as constants, with activation energy constants left as zero. If the user wishes TOXI4 to determine rates, based on the temperature-based Arrhenius function, then non-zero activation energies specified as constants will cause a set calculation to be performed for each rate constant. Alternatively, activation energies may be specified for each ionic species and hydrolysis reaction (acid, neutral, base) simulated. Without this specification, rate constants are not adjusted to ambient water temperatures. TOXI4 handles photolysis by calculating a first-order rate coefficient from the absorption rate and quantum yield for each ionic species and phase. The user may specify that the model calculate the rate constant or the user may provide a near-water-surface rate. TOXI4 is presently designed to handle aquatic systems, rather than CDF environments. Rates for degradation under CDF conditions will have to be determined to examine the utility of TOXI4 for CDFs.

81. Present information on degradation of organic compounds is primarily concerned with processes occurring in water, soil, or sediment. CDFs are unique environments in that their substrates undergo a transition from aquatic to terrestrial ecosystems. Degradation mechanisms occurring in CDFs should not differ from what is known to occur in other water, soil, and sediment systems. However, few, if any, studies on biodegradation of organic contaminants have been conducted on CDFs, and current understanding of the processes occurring must be inferred from what is known about other water, soil, and sediment systems. Moreover, there is no understanding of the contribution made by degradation mechanisms to the mass balance of organic contaminants in CDFs.

82. Initially, the relative importance of degradation of organic contaminants to the mass balance of contaminants through time at CDFs must be assessed. If the contribution of degradation processes to the mass balance over time is significant, then CDF-specific procedures for assessing rates of decomposition resulting from microbial, hydrolytic, and photolytic processes must be developed. These procedures should be formulated in a manner that will permit Corps field offices to determine degradation rates under varying environmental conditions within the CDF, including degradation within the dike

structure itself. It is possible that the CDF itself may serve as a biological treatment facility.

### Microbial Transformations of Metals

83. Microbial transformations of metals involve alterations in valence or changes from inorganic to covalently linked organic forms; these do not include precipitations as hydroxides or sulfides or chelation of inorganic species not resulting in changes in valence. Metal transformations can be divided into the following two major categories: (a) conversions resulting from oxidation-reduction processes acting on inorganic forms; and (b) inter-conversions between inorganic and organic forms, particularly methylation and demethylation. The methylated forms of metals are generally more toxic than their demethylated counterparts. Summers and Silver (1978) summarize bacterial transformations of metals as follows:

<u>Process</u>	<u>Target Metals (Valence)</u>
Oxidation	As(III), Fe(0), Fe(II), Mn(II), Sb(III)
Reduction	As(V), Fe(III), Hg(I), Hg(II), Mn(IV), Se(IV), Te(IV)
Methylation	As(V), Cd(II), Hg(II), Pb(II), Se(IV), Sn(II), Te(IV)
Demethylation	RHg(II), where R = methyl or ethyl group

84. Much of what is known about metal transformations has been developed through research conducted on reclamation of metals from low-grade ores and in the formation of acid mine drainage (Dugan 1972; Lundgren, Vestal, and Tobita 1974; Summers and Silver 1978). Extensive work has been done on the biotransformations of iron and manganese (Neilands 1974; Summers and Silver 1978; Ehrlich 1981). Much of the more recent research has focused on the biochemical and genetic properties of microorganisms actively interacting with the metals. The importance of microbial transformation reactions within the CDF environment has not been assessed. Based on what occurs in the natural environment, such transformations become significant only in areas where metal deposits are concentrated. Some CDFs may have high levels of metals if they contain sediments contaminated with wastes released by industries concerned with plating, battery production, or metal production. However, whether or not the concentrations of metals in these sediments are sufficient to support high levels of microbial activity is not known. Thus, the significance of microbially mediated metal transformations in CDFs is uncertain.



85. One related process that does not involve microbial transformation of metals, but may nonetheless mobilize metals, is chelation. Certain dissolved organic substances, such as humic acids, are produced during natural microbial degradation of organic matter. These substances have the capacity to sequester, or chelate, metals in the surrounding environment. Chelation is known to mobilize iron and other metals in aquatic ecosystems. However, the importance of chelation as a mechanism for mobilization of metals from CDFs has not been assessed, and no estimates of the amounts of metals that may be released in this way are available.

#### Mobilization of Contaminants by Microorganisms

86. Microorganisms are capable not only of degrading contaminants to simpler compounds that are more mobile, but also of subtly modifying the chemical structure to produce compounds that are potentially less mobile. Either of these pathways possesses significance in the internal cycling of contaminants within a CDF, and may have significance for net mass balance. Unfortunately, this is an area that has not been examined for sediments in a CDF environment. Effects of such processes on contaminant mobility, other than for the production of organic compounds that can complex with contaminants and mediate transport by rendering them more soluble, remain unclear.

87. No laboratory tests or models exist for predicting the overall effects of the many potential microbial pathways for contaminants in a CDF. A method should be developed for making at least a crude estimate of the relative significance of microbial processes to net mass losses of contaminants from CDFs.

#### Plant Uptake

88. Colonization of a CDF by plants results in many modifications of the CDF that can indirectly affect contaminant loss. For example, light and air movement are restricted beneath even a low vegetative canopy; therefore, temperature and evaporation rates are reduced. Litter accumulation can decrease surface runoff and soil temperature, and increase soil organic matter. These changes affect water movement through the dredged material, pH,

and microbial populations, all of which potentially affect contaminant movement and eventual loss.

89. During early stages of filling, colonization of a CDF by plants depends upon site construction and filling practices, especially elevation, as well as particle size of the dredged material, rate and degree of compaction and dewatering, availability of plant propagules, and, in some cases, salinity (Landin, Webb, and Knutson 1989). As soon as areas are created that are sufficiently shallow for plant growth, other conditions being favorable, colonization begins and proceeds within constraints of individual site characteristics and locations. Colonization may be typical of primary succession in the region as has been observed in long-term monitoring of some CDFs (Landin, Webb, and Knutson 1989).

90. Pioneering species, which often colonize some areas of the CDF within the first few months of dike construction (Landin, Webb, and Knutson 1989), must be adapted to survival under extreme conditions, e.g., a saturated, anoxic substrate and/or high salinity. Frequently, algae and submerged and emergent aquatic vascular species are the first to colonize the CDF. If the colonized area remains undisturbed, pioneering species may give way to later successional species. Topography of the CDF during filling depends primarily upon the design and subsequent use of the site. However, pioneering plant species tend to ameliorate extreme site conditions, even disturbances, creating a more favorable habitat for succeeding colonizers. For example, emergent vegetation on the aquatic fringe of a predominantly aquatic site holds sediment and eventually accumulates decomposed organic matter, resulting in sediment accretion. Emergence of sediment from the water results in increased aeration, leaching of salts and certain minerals and metals, and changes in pH. Such changes may result in new habitat for lowland shrubs and trees, while also opening new avenues of mobility for contaminants.

91. Physical and chemical characteristics of the CDF, which change during active filling due to consolidation and dewatering of the dredged material, also affect the suitability of the habitat for plants. As filling of the CDF proceeds, new areas for pioneering species are formed and successional patterns in other areas may be disrupted. Consequently, the plant community of a CDF may remain highly dynamic long after all filling has ceased.

## Heavy metals

92. Natural physical and chemical processes dominating marsh soil-water systems, which are common within CDFs during early stages of filling, seem to effectively immobilize nickel, zinc, cadmium, chromium, and lead to insoluble soil fractions, thereby reducing the transfer of these metals from freshwater marsh substrates to vascular vegetation (Lunz 1978). However, placement of dredged material into an upland (oxidized) environment changes the bioavailability of several metals, e.g., cadmium, zinc, copper, and lead, due to transition of the sediment from anaerobic to aerobic (Gambrell et al. 1977). The two heavy metals, cadmium and mercury, have received the greatest attention because they potentially pose the greatest human health risk from a water quality perspective (Peddicord et al. 1986). Zinc, copper, and lead pose much less risk to water quality, even though they are mobilized by plants (Chaney 1975; Gambrell et al. 1977; Folsom, Lee, and Bates 1981; and Lee, Folsom, and Bates 1983). Studies of plant uptake of other metals that are relevant to CDFs, e.g., arsenic, nickel, and chromium, are limited. However, Folsom and Houck (1990) have developed a computerized procedure for predicting plant uptake of a suite of heavy metals from contaminated freshwater dredged material. Plant uptake of cadmium and mercury are discussed below since they possess the greatest potential for ultimate risk if transported from the CDF, and because more is known about their mobilization from soils/sediments by plants.

93. Cadmium. When marsh substrates oxidize, the cadmium content of aboveground plant tissue has been shown to increase consistently and substantially in *Distichlis spicata*, *Spartina alterniflora*, and *Sorghum halepense* in both laboratory and greenhouse studies (Gambrell et al. 1977). Folsom, Lee, and Bates (1981) demonstrated that cadmium content in tissues and tubers of *Cyperus esculentus* grown in upland (oxidized) sediment increased compared with the same sediment maintained under flooded (reduced) conditions. Simmers et al. (1981) have also shown that the cadmium content of *Cyperus* spp. was greater under oxidized than under reduced conditions in both a natural marsh and when the plants were grown in the marsh sediment in a greenhouse.

94. Accumulation of cadmium in plant shoots has been related to ionic activity, soil pH, and soil organic matter content. Checkai, Corey, and Helmke (1987) reported highest uptake of cadmium by plant shoots at low cadmium-ion activity, which suggests that cadmium is taken up by a metabolically active mechanism. A change in soil pH from 6.5 to 5.5 can more than

double the cadmium level in crop plants (Chaney 1981). As dredged material placed in an upland setting oxidizes, the pH drops, often dramatically. Therefore, plant uptake of cadmium is especially likely in oxidized CDF sediment that has decreased in pH. High organic carbon content in sediments (Folsom, Lee, and Bates 1981), as in soils (Chaney 1981), can act to reduce cadmium uptake by plants.

95. Mercury. Hogg, Bettany, and Stewart (1978) demonstrated accumulation of mercury in brome grass (*Bromus inermis*) roots; however, only small quantities were translocated to aboveground plant parts. Similar results have been reported for the salt-marsh plant *Spartina alterniflora* (Kraus, Weis, and Crow 1986; Newell, Hicks, and Nicora 1982; and Breteler, Valiela, and Teal 1981) and for the aquatic plant *Salvinia natans* L. (Sen and Mondal 1987). Kraus, Weis, and Crow (1986) found that hydathodes (salt-excreting organs) of *Spartina* leaves contained 5-1/2 times more mercury than is typical in sea salts. Apparently, the same mechanisms utilized by *Spartina* to regulate internal salt levels and salt tolerance function in the elimination of ionic forms of mercury.

#### Organic contaminants

96. Plant uptake of organic contaminants from soils depends upon the physicochemical characteristics of the contaminant, properties of the soil in which the contaminant occurs, and the physiology of the plant species. In general, compounds that are soluble to slightly soluble in water possess the greatest potential for being swept into the plant via its aqueous transport system. Compounds that are only sparingly soluble or are insoluble possess potential for partitioning with lipid portions of the plant root. In addition to aqueous solubility, the  $K_{ow}$  of a compound is often used to indicate the lipophilicity of the compound, or the potential the compound possesses for preferentially partitioning into fatty organic tissues. The  $K_{ow}$  is a measure of the relative preference the compound has for octanol, an organic solvent, as opposed to its preference for water. Contaminants having a low  $K_{ow}$  (<1.0) prefer aqueous systems while those having a high  $K_{ow}$  (>1.0), prefer lipid systems. Many of the organic contaminants of concern in CDFs have a high  $K_{ow}$ .

97. The persistence of the contaminant in the environment is also important to its potential for plant uptake. Compounds that are very volatile may escape faster than they are translocated by plants. In general, Ryan et al. (1988) submit that compounds with half-lives greater than 6 months (or

greater than the growing season of the plant) persist long enough to impact plants.

98. Soil properties that potentially affect plant uptake of organic contaminants include organic matter, clay content, and soil water content. Soil organic matter and clay compete with lipophilic plant tissues for lipophilic organic contaminants. For example, in greenhouse studies with 2,4,6-trinitrotoluene (Folsom et al. 1988), a sparingly soluble organic compound, plant growth was significantly greater in a soil that was high in organic carbon and percent clay than in a soil that was low in both parameters. The difference was attributed to soil adsorption of TNT by the organic carbon and clay. Adsorption of TNT has also been highly correlated with clay content in soils by Pennington (1988). For compounds transported in the aqueous phase, increases in soil moisture can increase plant uptake. For example, Walker (1971) found that increases in soil moisture content caused increases in the phytotoxicities of several herbicides because of increased transport of herbicide into the plant. If the CDF is colonized by plants during early stages of filling, mobility of the more water-soluble contaminants may increase.

99. Plants exhibit a wide range of physical and physiological characteristics that affect their ability to take up organic contaminants. Plants with high water content and rapid transpiration rates transport large quantities of water. If contaminants are water soluble, they may become concentrated in such plants. Some plants possess oily cuticles and/or oil cells on roots or aboveground parts that provide a compartment for the partitioning of lipophilic contaminants from the soil or from the air. Such species differences among plants result in differing capacities for taking up organic contaminants.

100. Ryan et al. (1988) have proposed a method of evaluating the plant uptake potential of neutral or weakly ionized organic compounds from soils. The method allows grouping of chemicals by their relative potential for plant uptake based on physicochemical parameters. Concentration factors, which are usually defined as the ratio of the concentration of the contaminant in the plant, or in a specific plant part, to the concentration in the soil, are used to explore the relationships among plant uptake, octanol-water partition coefficient ( $K_{ow}$ ) of the contaminant, soil organic matter, and soil water content. The authors conclude that compounds with a log  $K_{ow}$  of 1 or 2 are most likely to exhibit a significant transport to aboveground plant tissues,

while compounds having a  $\log K_{ow}$  greater than 5 would not be expected to move into aboveground plant tissues due to soil adsorption of the compounds. However, even compounds having a low  $\log K_{ow}$  may not be translocated if metabolism occurs in the roots.

101. Ryan et al. (1988) also addressed vapor phase plant uptake of organic contaminants. The authors use a Henry's Law constant ( $H_p$ ) of  $10^{-4}$  as a transition point between primary movement in solution and vapor phases and conclude that compounds having an  $H_p$  greater than  $10^{-4}$  have potential for vapor phase uptake by plants. Some PCBs can be taken up from the air (see PCBs below). In addition to uptake directly from the air, organic contaminants may enter plants through the leaves following aerial deposition onto leaf surfaces (see PCBs below). Using as criteria the  $\log K_{ow}$ , environmental half-life, and  $H_p$ , a list of 107 priority pollutants was reduced to 50 having potential for plant uptake and translocation without vaporization (Ryan et al. 1988). None of the PCBs and only one of the PAHs (naphthalene) appeared on the list.

102. Boersma et al. (1988) have developed a theoretical model to describe transport of organic chemicals in plants. The model separates the symplastic, or living, transport system of the plant from the apoplastic, or nonliving, transport system. Although the test species was soybean, the authors assert that the model can be parameterized for most terrestrial vascular plants. The model mathematically defines two-compartment transport across various plant membranes and, using estimates of transport system volumes and flow rates, describes internal partitioning of the contaminant among plant compartments. Additional verification of the model with experimental data in order to determine structure/activity relationships between chemicals and their physical and physiologically controlled movement in plants is underway. If such models can be verified empirically, predicting plant uptake of organic contaminants at CDFs may be possible. Until plant uptake of organic contaminants is adequately quantified, its relative importance to other cycles within CDFs will be difficult to assess.

103. PCBs. Both plant uptake through roots and uptake through leaves following aerial deposition onto leaf surfaces have been demonstrated for PCBs. Root uptake of PCBs has been seen in soybeans (Worobey 1984), purple loosestrife (Bush et al. 1986), potatoes (Gosselin, Naylor, and Mondy 1986), and beets and turnips (Sawhney and Hankin 1984). However, root uptake is not necessarily followed by translocation to upper portions of the plant. In

sewage sludge-amended soil containing 1.5 ppm PCBs (Aroclors 1016, 1242, and 1254) Gosselin, Naylor, and Mondy (1986) found limited uptake by potatoes (0.04  $\mu\text{g/g}$ ) with the PCBs concentrated in the peel. PCB levels in potato pulp and leaves were below detection. In a field treated with 100-ppm Aroclor 1254, Iwata, Gunther, and Westlake (1974) found that carrot root uptake ranged from 3 to 4 percent of that found in an equal weight of soil for one component of the Aroclor to from 30 to 50 percent of that found in the soil for another component (four congeners were seen on the gas chromatogram). Ninety-five percent of the PCBs taken up by the carrot roots were concentrated in the peel (leaves were not examined). Fries and Marrow (1981) found no evidence of translocation of PCBs (individual congeners) from roots to leaves of soybeans. They concluded that plants grown on PCB-contaminated soil would not be contaminated by translocation from the roots to the leaves. Nevertheless, implications for contamination of organisms that feed on roots of plants may be great.

104. Streck and Weber (1982) performed a statistical analysis of PCB plant uptake data from the literature. Plants included carrot, fescue, radish, soybeans, spruce, sugarbeets, tomato, and unidentified weeds. Soil treatments ranged from 0.046 to 100 ppm PCBs and soil levels at harvest ranged from 0.040 to 76 ppm. Plant uptake ranged from 0.0016 to 13.9 ppm with an average of 1.241 ppm. In spite of the wide range in experimental conditions, several factors seemed to exert a significant impact on plant uptake. The factors were plant species, degree of chlorination of the PCB, i.e., lower chlorinated congeners were more easily taken up than the higher chlorinated congeners (Iwata, Gunther, and Westlake 1974; and Suzuki et al. 1977), and growth period, i.e., PCBs tended to accumulate with time (Bush et al. 1986). PCB content in the plants also seemed dependent on soil concentration (Streck and Weber 1982).

105. Plant uptake of PCBs following aerial deposition has been reported (Moza et al. 1976; Weber and Mrozek 1979). The plant cuticle contains lipophilic compounds capable of capturing PCB fallout; however, as pointed out by Streck and Weber (1982), much of the captured contaminant may simply adsorb to the outer surfaces of the plant rather than move into the plant. Surface adsorption with or without plant uptake carries implications for cycling of contaminants into the litter fall of the CDF (see later section on ecological significance of plant uptake) and for contamination of grazing wildlife.

Greater consideration should be given to the role of aerial deposition of PCBs.

106. Although apparently dominated by root uptake, uptake of PCBs directly from the air has also been observed. Fries and Marrow (1981) found that foliar contamination of soybeans occurred from vapor sorption. Bush et al. (1986) found that all of the PCBs present in ambient air (concentrations of 140 ng/m<sup>3</sup>) were scavenged by purple loosestrife. Bush et al. (1986) did not distinguish between leaf surface adsorption and absorption into the plant.

107. Travis and Arms (1988) defined a relationship between  $K_{ow}$  for a number of organic compounds (including Aroclor 1254) and a bioconcentration factor for aboveground plant parts. The relationship was determined by correlating literature data for plant uptake with  $K_{ow}$ . They found that bioconcentration, i.e., the ratio of the concentration in the plant to the concentration in the soil, was inversely proportional to the square root of the  $K_{ow}$  ( $n = 29$ ,  $r = 0.73$ ). They suggest that this general relationship can be used to predict plant uptake of organic compounds in the environment. However, basing predictions on a relationship defined by an  $r$  of only 0.73 should be made with caution. Application of the relationship to Aroclor 1254 suggests very limited plant uptake potential.

108. PAHs. Some evidence in the literature supports growth stimulation of plants by polynuclear aromatic hydrocarbons (PAHs). Graf and Nowak (1966) report an increase in cell size for the algae *Chlorella*, *Scenedesmus*, and *Ankistrodesmus* grown in hydroponic cultures of six PAHs (3,4-benzopyrene, 1,2-benzanthracene, 1,12-benzoperylene, fluoranthene, 3,4-benzofluoranthene, and indeno(1,2,3,cd-pyrene). Deubert et al. (1980) also demonstrated increased root growth in corn and wheat treated with benzo[a]pyrene. Plant uptake through the roots appears to be limited (Deubert et al. 1980; Thomas, Ruhling, and Simon 1984), but has been found in carrots and lettuce. Siegfried (1975) found an average of 0.75 ppb 3,4-benzopyrene in head lettuce grown on garbage compost having an average concentration of 0.75 ppb. Siegfried (1975) found an average of 0.12 ppb benzopyrene in washed carrots, with 70-75 percent contained within the peeling.

109. According to Borneff et al. (1968), plants are capable of biosynthesis of PAHs. They assert that plants have a "normal" PAH level averaging about 10 µg/kg of benzo[a]pyrene, but conclude that the concentration in plants is insufficient to cause carcinogenesis in humans or animals consuming them.



110. Information for assessment of the relative importance of PAH contamination at CDFs is unavailable. Local industries probably exert a significant effect on PAH contamination at specific CDFs, but no data are available. For CDFs in the vicinity of the Great Lakes where atmospheric fallout and precipitation are major sources of PAHs (Eadie 1984), plants as well as sediments within CDFs may be affected.

#### Ecological significance of plant uptake

111. The ecological significance of plant uptake of contaminants has not been adequately researched. Not only does the potential exist for plants to serve as an avenue for contamination of higher organisms, including man, through the food chain, but plant uptake may make a significant contribution to other contaminant mobility pathways within a CDF, such as surface runoff, volatilization, and microbial degradation.

112. One example of the interaction of plant uptake with other contaminant cycles which has been explored by Kay, Scholten, and Bowmer (in preparation) and Marquenie, Simmers, and Kay (1987) is the concentration of metals in the surface layer of dredged material in a CDF by decaying, contaminated plant material. Kay, Scholten, and Bowmer (1988) found that concentrations of cadmium and zinc were greater in the leaf litter than in the dredged material beneath poplar trees growing on a dredged material disposal facility in The Netherlands. The latter authors report greater concentrations of magnesium, potassium, titanium, vanadium, manganese, barium, and cadmium in woodland topsoil than in underlying layers at Times Beach CDF, Buffalo, NY. Both reports suggest that such contaminated surface layers potentially contribute to elevated concentrations of certain heavy metals, e.g., cadmium, in earthworms and thus provide a mode of entry of metals into food webs. The implication of translocation of metals and perhaps organic contaminants from dredged material by plants with subsequent concentration in surface soils should be investigated further. However, recycling to the surface may result in more rapid degradation of contaminants due to exposure to an aerobic environment and to sunlight. The significance of interactions of this cycle with other pathways of contaminant mobilization other than the food web should also be evaluated.

113. Presently, insufficient data exist to evaluate mobilization of organic contaminants from dredged material by plants, or the significance that plant uptake of organic contaminants has on contaminant cycling or the food

chain. Although an attempt to model plant uptake of organic chemicals has been made (Boersma et al. 1988), sufficient data are lacking for comprehensive verification of the model.

114. The colonization of CDFs by native plants potentially contributes to the cycling of contaminants indirectly even when contaminants are not mobilized by the plants. For example, root growth changes the texture and chemistry of the soil, the presence of plants influences the movement of soil particles by wind and water, and plants increase the pool of organic material to increasing depths as the CDF ages. Plants also provide habitat that encourages colonization by burrowing and foraging animals and by birds. The presence of these animals also has the potential for influencing the mobilization of contaminants. Much is known concerning the interrelationships of plants, soils, and animals. However, sufficient information does not exist to determine the magnitude of this pathway in mobilizing contaminants. Due to the dynamic nature of plant colonization in CDFs and differences in uptake characteristics among plant species, contaminant mobilization by plants can be expected to depend upon the stage of CDF filling. Species diversity of the plant communities as well as local climate would further complicate model calculations.

115. Freshwater plant uptake data from previous studies are being used to develop a first-generation predictive model of plant uptake of heavy metals under a Long-Term Effects of Dredging Operations Program work unit. The initial emphasis of this model will be to predict heavy metal uptake from freshwater upland and wetland dredged material disposal sites. Incorporation of bioassay results into a predictive model followed by verification of this and other such models will permit the assessment of the relative importance of plants to heavy metal contaminant cycling within CDFs. However, the effort should be expanded to encompass organic contaminants, plant species differences, and plant uptake in saline systems.

#### Effects of Animals on Contaminant Cycling

116. An evaluation of mass balance of contaminants within food webs on CDFs not only requires information on contaminant uptake by members of the food web, but also requires knowledge of the transfer mechanisms for contaminants among animals within the food web, and quantitative data on total biomass and biomass transfer among animals. The biomass and diversity of

ecosystems developing on CDFs are likely to be unique to the site; therefore, accurate assessment of contaminant concentrations will very likely require a population inventory for each CDF. Nevertheless, generalizations for the sake of estimating the relative importance of animals to mass balance, assuming some specific habitat diversity, may be warranted.

117. Perhaps the most extensive overview of ecosystem development and contaminant concentrations within a CDF is provided by studies of Times Beach CDF, Buffalo, NY (Stafford et al., in preparation). Results suggest that heavy metals are the most persistent and mobile contaminants in the CDF and that low-molecular-weight organo-chloride compounds volatilized or effectively disappeared from the site via other mechanisms over time (Simmers et al. 1987). Marquenie, Simmers, and Kay (1987) in a study of Times Beach concluded that none of the organic compounds present in the sediments moved through the food chain to birds and mammals since none were found in bird or mammal tissues. However, Kay, Simmers, and Marquenie (1986) found that PCB levels in fish were sufficiently high to preclude human consumption until more exhaustive evaluations were concluded. All results given for the Times Beach CDF are based on data collected over a 2-year period or less, commencing about 5 years after dredged material placement ceased.

118. A closer look at contaminant cycling potential can be gained by examining contaminant uptake by animals occupying lower trophic levels of the food web at the Times Beach CDF. Carnivores and detritivores within lower trophic levels, e.g., spiders and earthworms, accumulated greater concentrations of heavy metals than did herbivores, e.g., mice. Movement of lead, nickel, and chromium from the dredged material through the food web within the upland ecosystem was greater than the movement of zinc, copper, and cadmium.

119. Estimation of the maximum PCB body burden that aquatic organisms could receive from contaminated sediments at CDFs is possible. The estimate is based on sediment chemistry and equilibrium partitioning of chemicals among all the discrete compartments of a system (sediments, water, biota, etc.) according to chemical potential or activity in each (McFarland 1984; Lake, Rubinstein, and Pavignano 1987). The estimation equation is as follows:

$$WBP = 3.00(Cs/foc)(f1) \quad (11)$$

where

WBP = whole-organism bioaccumulation potential (as PCB content, ppm, fresh weight)

Cs = PCB concentration in sediment, ppm, dry weight basis

foc = sediment organic carbon, decimal fraction

fl = organism lipid, decimal fraction

For confined ecosystems such as CDF ponds or small lakes, an assumption of steady state is considered a usable simplification (Clarke, McFarland, and Dorkin 1988; ENSCO 1988). The calculations are simple, but require that organic carbon content of sediments as well as PCB concentrations be reported. Estimations can be made using the procedure described in McFarland and Clarke (1987) and known lipid content of fish or other aquatic fauna of interest. A preference factor for PCB equilibrium distribution between sediment organic carbon and organism lipid has also been determined using results of laboratory and field experimentation (McFarland and Clarke 1986).

120. More information is needed to assess the relative importance of animal uptake to internal cycling of contaminants within CDFs. Some of the information available in the literature may be applicable, but much more must be learned about uptake of contaminants by animals at CDFs, as well as about CDF population dynamics and biomass production.

## PART VI: SUMMARY

121. Evaluation of the magnitude of contaminant migration, cycling, and mobilization pathways in a CDF is essential. Evaluation needs include assessment of the relative significance of the various pathways and development of methods for computing pathway mass balances. The present information does not permit evaluation of the relative significance of contaminant transport pathways from a CDF. Pathways involving movement of large masses of water, such as CDF effluent, leaching through permeable dikes, or leaching through the dredged material, have the greatest potential for moving significant quantities of contaminants out of the CDF. Pathways such as volatilization may also result in movement of substantial amounts of volatile organic contaminants from CDFs. The relative importance of contaminant cycling and mobilization pathways to net mass balance has not been determined. Available information on each of the contaminant migration, cycling, and mobilization pathways is summarized in Table 1. Where possible, methods for making rough estimates of contaminant mass movement via pathways has been provided in the test.

122. Methods for computing mass balances for contaminant migration, cycling, and mobilization pathways are needed for a comprehensive analysis of migration pathways in CDFs. Existing procedures give crude estimates for some pathways. The framework for tying together contaminant migration, cycling, and mobilization pathways will be developed during the next fiscal year. This framework will be in the form of a tiered assessment.

Table 1  
Status of Available Information on Contaminant Migration, Cycling,  
and Mobilization Pathways

Pathway	Status
CDF Effluent	Empirical methods exist for assessing CDF effluent
Water transport through permeable dikes	Methods for making crude estimates that do not account for many of the variables affecting this pathway have been used
Leaching	Methods are under development
Volatilization	Unverified predictive equations have been formulated
Surface runoff	Empirical methods have been developed
Degradation of organic contaminants	No information is available from CDFs, but much work has been conducted in soils and sediments
Microbial transformations of metals	Importance in a CDF environment has not been shown
Mobilization by microorganisms	Almost no information is available
Plant uptake	Predictive models have been developed for metals under certain conditions; limited information is available in the literature for organic contaminants
Animal uptake	Limited information is available for CDFs; no predictive models are available for CDFs

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